## Catalytic Dehydrogenation of Alkanes Using Pincer Ligand Complexes

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The functionalization of unreactive hydrocarbons is a challenging problem that was recognized over twenty years ago.<sup>1,2</sup> The dehydrogenation of alkanes to alkenes has important applications in the production of bulk precursors for polymer production and organic synthesis.<sup>3,4</sup> The current industrial procedure for dehydrogenation of alkanes involves a mixture of substrate and water in the gas phase at temperatures of 600 °C over a heterogeneous iron oxide catalyst.<sup>5</sup>

Many attempts to convert both straight chain and cyclic alkanes to their corresponding alkenes with homogenous catalysts resulted in poor selectivity and low turnover numbers, eg. <10, due to catalyst decomposition at the temperatures required for alkane C-H bond activation.<sup>1,2,6,7</sup> Sacrificial hydrogen acceptors, such as 3,3-dimethylbutene(tbe), were also required to prevent the hydrogenation of the product alkene.<sup>1,2</sup>

These problems of the catalyst instability and the equilibrium barrier have prompted efforts to develop more reactive transition metal complexes to facilitate the dehydrogenation of alkanes. A breakthrough occurred with the 1996 report of especially active and stable catalysts involving rhodium and iridium complexes of a pincer ligand.<sup>8</sup> Pincer ligands of the type shown in Figure 1, are tridentate ligands that bind to the metal through either a metal carbon bond, and two dative bonds, or three dative bonds from heteroatom substituents.



Figure 1. Various pincer ligands

This coordination mode stabilizes the metal carbon bond in transition metal complexes.<sup>9</sup> By employing bulky R groups such as 'Bu, or 'Pr on the heteroatom, stable complexes of highly reactive species can form without oligomerization or decomposition.

Pincer ligand complexes of rhodium and iridium as catalysts for the dehydrogenation of alkänes are receiving widespread attention.<sup>10-12</sup> The use of compounds such as (PCP)MH<sub>2</sub> (PCP= $C_6H_3(CH_2PBu_2^i)_2$ -2,6) (M=Rh, Ir) (1a, Ib) dehydrogenate various cycloalkanes to cycloalkenes at 200 °C with turnovers of 70-80 turnovers/h (Figure 2). The reaction proceeds at 200 °C in neat solvent and without the use of a sacrificial hydrogen acceptor such as *tert*-butyl ethylene.



Figure 2. Dehydrogenation of cyclooctane using (PCP)Ir(H)<sub>2</sub>

The mechanism by which the dehydrogenation is carried out is not understood. Both experimental and computational studies have been conducted in order to elucidate the mechanism.<sup>13-16</sup> The initial process appears to be loss of H<sub>2</sub> to form the intermediate 'Ir{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PBu<sup>t</sup><sub>2</sub>)<sub>2</sub>-2,6}' Figure 3. This is formally a 14 electron species, however the possibility of agostic interactions with solvent or the phosphine alkyl groups has not been ruled out. The bulky phosphines prevent dimerization, and allow for C-H bond activation of the alkane solvent. This produces a 16 electron alkyl hydride, which undergoes  $\beta$ hydride elimination to produce an 18 electron metal alkene complex. Loss of the alkene results in regeneration of the catalyst.



Figure 3. Loss of hydrogen by (PCP)MH<sub>2</sub> to form 14 electron '(PCP)M'

Computational studies have also shown the dissociative pathway to have a lower Gibb's free energy than the associative pathway. These studies have led to the result that the mechanism of  $(PCP)Ir(H)_2$  dehydrogenating alkanes may have the loss of H<sub>2</sub> as the rate limiting step.

The use of  $(PCP)M(H)_2$  complexes as dehydrogenation catalysts is not limited to alkanes. Substrates containing functional groups such as alcohols and amines, have been dehydrogenated to produce ketones, aldehydes, and imines.<sup>17,18</sup> Use of ethylbenzene as substrate produces styrene at a rate of 50 turnovers/ hour.<sup>19</sup>

Structural information of  $(PCP)MH_2$ , as well as mechanistic studies of its use in the dehydrogenation of alkanes is important in developing better catalysts for alkane dehydrogenation. The industrial applications of these catalysts for the production of bulk precursors, especially for the selectivity of terminal alkenes over the thermodynamically favored internal alkenes, as well as possibilities for hydrogen storage are enormous.

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